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COLOR OF PORCELAIN CONTAINING NEODYMIUM OXIDE

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The mechanisms of color formation in porcelain containing neodymium oxide, which can change the color by means of the absorption or reflection spectra, depending on the light source, are studied. The optimal content of neodymium oxide in porcelain is determined in the 1976 CIE system, the optimal neodymium oxide content in porcelain is determined, and the dependence of the color of articles on the firing medium and light source is determined.

Among the many groups of porcelain articles, hard porcelain with different variants of decoration is now widely used. Artists and designers who use hard porcelain need subglaze paints and pigments, which are also used for coloring ceramics. The number of articles (mainly articles manufactured abroad) with a colored ceramic mass — both single-color and with color variations (the interior of an article is one color and the exterior is a different color) — is continually increasing. Such porcelain is characteristic for china and large decorative interior articles (vases, pots for plants, plaques, panels, and so forth).

Oxides and pigments are used in subglaze decoration of porcelain. A few oxides are heat resistant in the firing temperature range of porcelain articles 1350 – 1410°C and in a reducing gaseous medium so that the subglaze color palette for hard porcelain is sparse. It is well known that chromium, manganese, and cobalt oxides withstand such firing conditions.

Pigments containing iron, titanium, copper, nickel, and other oxides as colorants are also used for subglaze painting on porcelain. High-temperature coloring compounds must be used for subglaze paints for solid porcelain. Such compounds are rare-earth element oxides (REEO). REEO can be used as components of paints for decorating porcelain articles and as a constituent of paste that can color porcelain. A pigment that can be used to color hard porcelain must meet two main requirements: it must be stable in the temperature interval 1300 – 1410°C and it must not change color in the range of the oxidation-reduction potential (ORP) of the gas medium used for firing porcelain.

It is known that ceramic pigments of the $Nd_2O_3 – Al_2O_3$ system are used as subglaze paints for porcelain and glazed pottery as well as in majolica. Such paints are heat resistant, withstand well firing temperatures in the range 1140 – 1350°C, do not give pinholes, dry areas, clumping, and other defects on glaze, and produce very pure and soft rose-lilac tones.

The process of synthesizing ceramic pigments with equimolecular ratios of the oxides ($Nd_2O_3 : P_2O_5$, $Nd_2O_3 : ZrO_2$, $Nd_2O_3 : TiO_2$) has attracted interest in recent years. For such oxide ratios it is possible to obtain pigments with different palettes suitable for coloring glazes [1].

The known temperature dependence of the standard value of the Gibbs formation energy of certain oxides possessing a coloring effect [2] makes it possible to evaluate the reduction of metal oxides in a gas medium with a high CO content (2 – 5%[2]). It is evident that REEO cannot be reduced by carbon monoxide, so that they are stable in the ORP range of the gas medium for firing solid porcelain.

The color of porcelain is determined by the properties of the pigments which are introduced into the porcelain paste. Each phase composition of porcelain is mainly represented by the glassy phase, so that it can be supposed that glass and porcelain with the addition of REEO have the same coloration mechanisms and correspondingly similar color characteristics. Glasses containing rare-earth oxides are distinguished by high light transmission in the visible part of the spectrum and color purity, and they possess a series of other valuable physical – chemical properties. Consequently, there is great practical interest in using REEO as pigments for household and artistic porcelain. Different variants of coloration of a paste by oxides of rare-earth elements, specifi-

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[2] Here and below — the mass content.

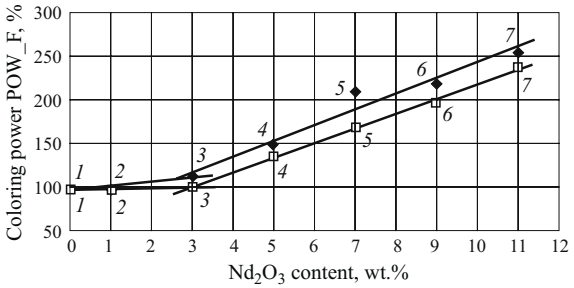

Fig. 1. Coloring power POW_F of neodymium oxide versus the neodymium oxide content in hard porcelain: ◆) coloring power for light source C; □) coloring power for light source A; *1*) standard sample FP; samples with Nd_2O_3 content: *2*) 1% (FPN-1); *3*) 3% (FPN-3); *4*) 5 % (FPN-5); *5*) 7% (FPN-7); *6*) 9% (FPN-9); *7*) 11% (FPN-11).

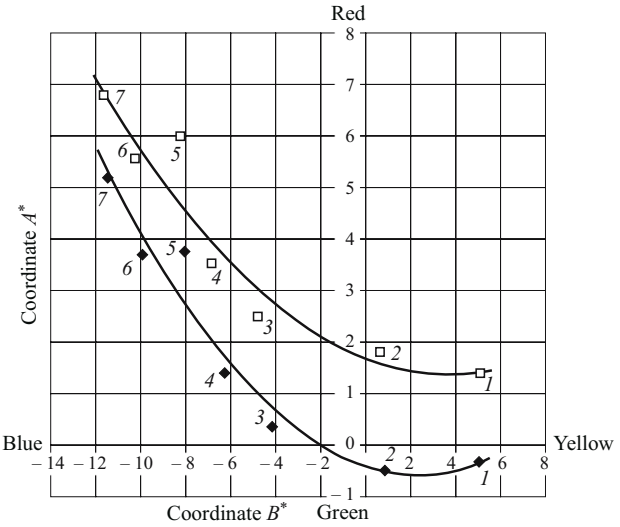

Fig. 2. Variation of the chromatic coordinates A^* and B^* of porcelain containing neodymium oxide for different light sources: ◆) chromatic coordinates with light source C; □) chromatic coordinates with light source A; *1*) standard sample FP; *2*, *3*, *4*, *5*, *6*, and *7*) samples containing Nd_2O_3: FPN-1, FPN-3, FPN-5, FPN-7, FPN-9, and FPN-11, respectively.

cally, neodymium oxide Nd_2O_3, were tested at the Ob"edinenie Gzhel' JSC.

The objective of the present work is to study the effect of neodymium oxide on the coloring characteristics of hard porcelain.

The reflection spectra of the samples were measured with a Pul'sar spectrocolorimeter in the wavelength range 380 – 720 nm. The Foton technical program system was to calculate the color characteristics.

We shall give the basic terms and indicators of the color characteristics used to calculate the concentration dependences of the neodymium oxide content in porcelain:

the relative coloring power POW_F of a colorant — a measure of its capability to impart color to the material and defined as the ratio of the concentration of pigments in colored and standard samples [3];

the color coordinates: luminance L^* and chromaticity from green — A^* to red A^* and from blue — B^* to yellow B^* in the 1976 CIE $L^*A^*B^*$ system [3].

Six experimental pastes based on the production paste (FP), used at Ob"edinenie Gzhel' JSC, with 1, 3, 5, 7, 9, and 11% Nd_2O_3 were prepared to study the coloring power POW_F of neodymium oxide. It was found that neodymium oxide is a weak pigment (Fig. 1): for 5% Nd_2O_3 the coloring power is 159.4%, whereas the coloring power of cobalt oxide with the same concentration is 2612.2%. The color indicators of porcelain containing neodymium oxide in the CIE $L^*A^*B^*$ system are presented in Table 1. It is evident that for light sources A and C the luminance of porcelain samples with the same neodymium oxide content remains constant with substantial variation along the coordinate *A* (Fig. 2). Such a shift from yellow-green color into the red-blue color equals 1.6 – 2.3 units depending on the content of Nd_2O_3; this is due to the nature of the light source A which is characterized by maximum emission in the red-yellow region of the spectrum.

The main coloring impurity in porcelain is iron, which changes the chromaticity of porcelain depending on the ORP of the gas medium. For example, the chromaticity coordinate B^* of FP porcelain samples (Fig. 3) fired in a gas medium

TABLE 1.

Porcelain sample	Nd_2O_3 content, wt.%	POW_F	Color coordinates with light source					
			C			*A*		
			L	*A*	*B*	*L*	*A*	*B*
FP	0	100.00	79.80	– 0.31	5.13	80.09	1.38	5.16
FPN-1	1	103.63	79.48	– 0.47	1.04	79.48	1.78	0.65
FPN-3	3	122.46	77.54	0.36	– 4.16	77.25	2.49	– 4.76
FPN-5	5	159.40	74.87	1.40	– 6.26	74.53	3.51	– 6.82
FPN-7	7	220.38	71.31	3.78	– 7.99	71.07	6.00	– 8.20
FPN-9	9	228.21	71.34	3.74	– 9.92	70.94	5.55	– 10.29
FPN-11	11	266.24	69.79	5.19	– 11.42	69.42	6.77	– 11.58

TABLE 2.

Porcelain sample	Dominant wavelength,* nm		Conventional light frequency,* %	
	Firing No. 1**	Firing No. 2**	Firing No. 1**	Firing No. 2**
FP	576.1	564.7	5.85	1.96
FPN-1	568.9	587.0	1.14	1.66
FPN-3	475.8	476.5	4.12	5.15
FPN-5	472.2	474.8	6.02	6.55
FPN-7	459.2	472.0	7.33	7.35
FPN-9	466.2	467.1	9.34	8.41
FPN-11	461.3	460.6	10.66	9.33

* Light source C.

** Firing No. 1 with a gas medium with average reducing power (≤ 2% CO), No. 2 with strongly reducing gas medium (≤ 3.5% CO).

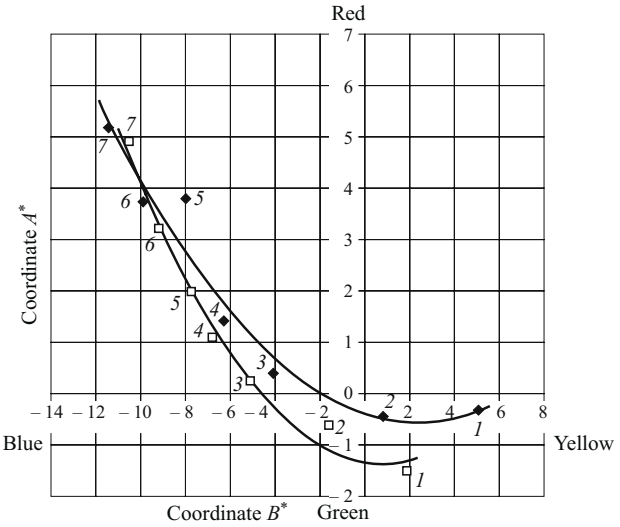

Fig. 3. Variation of the chromaticity coordinates A and B of porcelain containing neodymium oxide as a function of the firing conditions: ◆) firing in a gas medium with average reducing power (≤ 2% CO), temperature up to 1350°C; □) firing in a strongly reducing gas medium (≤ 3.5% CO), temperature up to 1410°C; the remaining notation is the same as in Fig. 2.

with average reducing power (≤ 2% CO) is 2.5 times greater than for samples fired in a strongly reducing gas medium (≤ 3.5% CO). When up to 9% of neodymium oxide is introduced into the porcelain composition (sample FPN-9) the chromaticity of porcelain depends on the ORP of the gas medium; this is explained by the combined coloring power of iron and neodymium oxides. For Nd_2O_3 content > 9% the main colorant is neodymium oxide and the dependence of the chromaticity coordinates on the ORP of the gas medium is negligible. A determination of the dominant wavelengths and the conditional purity of color according to a spectral chromaticity line with light source C (Table 2) showed that as the concentration increases, the dominant wavelength of porcelain samples containing neodymium oxide which were fired under different conditions shifts from the yellow region of the spectrum into the light-blue and blue – light-blue regions in a manner so that for 9% Nd_2O_3 it differs by 1 nm. The conditional color purity of porcelain samples reaches its lowest value for 9 – 11% Nd_2O_3. Aside from this, for different firing regimes FPN-5 porcelain possesses a smaller color difference ΔE ($L^*A^*B^*$), equal to 12.32, than porcelain containing 1% cobalt oxide, in which the color difference is 53.08.

Introducing Nd_2O_3 into the paste yields porcelain with different color depending on the light source. The expert method was used to determine that the preferred color of porcelain is reached for 5 – 7% Nd_2O_3. This agrees well with the data of [4, 5], where the optimal neodymium oxide content in glass is 4.3 – 7.5%. These data were used as a basis to prepare a porcelain paste based on the paste produced by Ob"edinenie Gzhel' JSC:

FP is the paste used to produce porcelain based on the following initial materials (%): 35 – 45 kaolin, 5 – 10 clays, 20 – 30 quartz sand, 20 – 30 pegmatite; the chemical compositions are presented in Table 3;

FPN-5 — experimental porcelain paste prepared using FP with 5% Nd_2O_3.

The color of thin layers of porcelain or porcelain with a negligible content of neodymium oxide ranges from violet to light-blue; for thick layers or high neodymium oxide concentrations the color ranges from rose to lilac. Visual perception of color changes depend not only on the thickness of the porcelain but also on the illumination. Consequently, porcelain containing neodymium oxide is perceived to possess color duality — dichroism, i.e., iridescence. The visual perception

TABLE 3.

Material	Content, wt.%								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	calcination loss
Prosyanovskoe kaolin	46.83	36.60	0.46	0.95	0.66	0.33	0.08	0.22	13.85
Chasov Yar clay	56.27	31.29	0.72	1.02	0.65	1.63	0.34	0.60	7.23
Quartz sand	99.77	–	0.002	–	–	–	–	–	0.20
Chupinskoe pegmatite	73.68	15.26	0.20	0.85	0.56	5.74	2.85	–	0.55

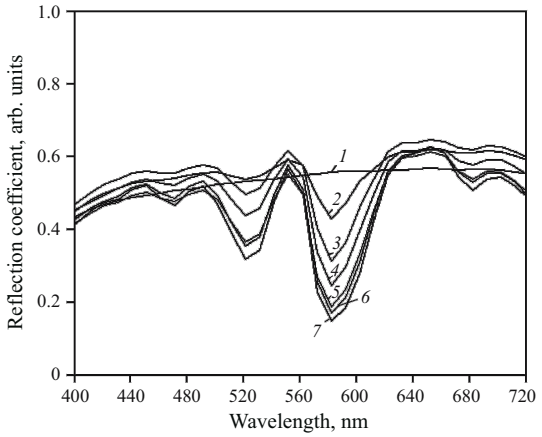

Fig. 4. Reflection spectrum of porcelain containing neodymium oxide: *1*) reference sample FP; samples with neodymium oxide content: *2*) FPN-1, *3*) FPN-3, *4*) FPN-5, *5*) FPN-7, *6*) FPN-9, *7*) FPN-11.

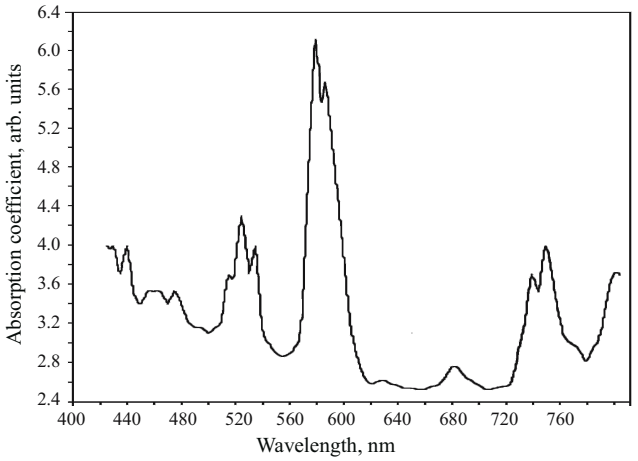

Fig. 5. Reflection spectrum of porcelain containing neodymium oxide.

of the color of porcelain strongly depends on the light source, i.e., for light source C (simulating daylight) — from violet to light-blue and for light source A (simulating the light from an incandescent lamp) — from rose to lilac.

A SPECORD M400 spectrophotometer with different color filters absorbing definite wavelengths was used to measure the absorption spectra in the visible range with different sources of light. Thus, with a blue light filter, which transmits 400 – 570 nm wavelengths and simulates daylight, the spectra of porcelain containing Nd_2O_3 show that light with wavelengths 443 – 555 nm (violet-blue light) 468 – 513 nm (blue, light-blue, and blue-green colors), and 537 – 571 nm (green and yellow-green colors) is reflected, i.e., color ranging from violet to light blue is observed when one of the indicated wavelengths predominates. Similar behavior is observed with a red filter, which transmits light with wavelengths 620 – 760 nm and simulates the average light from an incandescent lamp: the spectra obtained for porcelain containing Nd_2O_3 show that light with wavelengths in the intervals 430 – 453 nm (violet color), 614 – 737 nm (orange-red and red color) is reflected, i.e., when one of these wavelengths predominates a color ranging from rose to lilac, obtained by adding violet and red colors, is observed.

The peaks corresponding to minima in the reflection spectrum (Fig. 4) of porcelain with different neodymium oxide content are similar to the maxima in the absorption spectrum of the neodymium ion [6] and the absorption spectrum of porcelain containing neodymium oxide (Fig. 5). The shape of the curves of the reflection spectrum remains practically unchanged irrespective of the Nd_2O_3 content in the porcelain.

The color play is due to the selective absorption of light by a narrow but steep and strong absorption band, which lies in the wavelength range 568 – 614 nm and separates the visible spectrum into two parts — blue and red. Porcelain containing Nd_2O_3 is characterized by two absorption bands in the visible part of the spectrum: the first one lies in the green range (505 – 545 nm) and the second one ranges from the yellow-green to the orange range (568 – 614 nm). As a result, porcelain colored with neodymium oxide possesses violet and light-blue colors, which are formed by violet and light-blue spectra, and rose and lilac colors, which are formed by the red spectra [3].

A well-known feature of ion Nd^{3+} is the continuous absorption spectrum with two main peaks in the visible region of the spectrum. This is explained by the fact that the ions of rare-earth elements possess a narrow-band absorption spectrum due to the special structure of their shell. The number of electrons in the electronic shells determines the electronic configuration of the ion. For third-row free ions of rare-earth elements the electronic configuration is $4f^n 5s^2 5p^6$ ($0 < n < 14$, where n characterizes the number of electrons in an incompletely filled $4f$ electronic shell). For sufficiently low excitation energy (no more than 5 eV or 40000 cm^{-1}) the spectra of rare-earth ions are primarily due to transitions between the energy levels of the $4f$ configuration [7]. For free ions and ions in a spherically symmetric environment, these levels are determined by, first and foremost, electronic repulsion and spin-orbit and orbital interactions of the $4f$ electrons. These interactions and the energy levels due to them change little when the immediate surroundings of an ion of a rare-earth element change.

The presence of anions in the immediate surroundings of rare-earth ions does not have a unique effect on the $4f$ electrons, which are screened by the closed $5s$ and $5p$ shells, but still results in some splitting of the energy levels of the $4f^n$ electronic configuration, which is characterized by the so-called crystal-field parameters which depend on the structure of the surroundings of the rare-earth ion.

On account of the screening of the $4f$ shell from the surrounding fields due to the filled outer $5s^2 5p^6$ shell, narrow bands with a line structure can appear in the spectrum. Absorption bands arise when a rare-earth ion makes a transition

under the action of a photon into one of the excited states. The excitation depends on the number of electrons in the 4*f* shell. Each energy level of the Nd^{3+} ion is the total energy of the ion, i.e., the coulomb interaction energy of 57 electrons with the nucleus ($Z = 60$), their kinetic energy, and the coulomb and magnetic interaction of these electrons. The energy levels of a free neodymium ion are degenerate. This means that when a neodymium ion resides in vacuum several states differing by the spatial orientation of the angular momentum will possess the energy corresponding to a given energy level. However, when the ion resides in a crystal, the ion is in a nonuniform electric field created by the nearest-neighbor and distant ions or ion groups, which form the crystal (or glass), surrounding it [8].

Since for any temperature the particles forming a crystal execute a vibrational motion, the symmetry of the environment and the intensity of the crystal field are dynamical quantities. This determines the transition probability between levels and the broadening of spectral lines. For the Nd^{3+} ion, whose valence electrons do not participate in a covalent bond with neighboring particles, the broadening of the spectral lines is negligible. The probability of transitions between certain levels becomes substantial, so that the lifetime of an excited level can equal several microseconds [9].

Knowing the absorption spectra of porcelain, which contains an Nd^{3+} ion, and the maximum wavelengths at which absorption occurs, it is possible to calculate the excitation energy of electrons for certain wavelengths with peaks, equal to 462, 524, 534, 570, 576, 738, and 745 nm, which correspond to 2.671, 2.366, 2.322, 2.175, 2.152, 1.672, and 1.656 eV. According to the arrangement of the bottom energy levels of the free Nd^{3+} ion, a transition occurs from the level $^4I_{9/2}$ into the excited levels $^4G_{11/2}$, $^2G_{9/2}$, $^4G_{7/2}$, $^{2,4}G_{7/2,5/2}$, $^4S_{3/2}$, and $^4F_{7/2}$ in accordance with the indicated wavelengths. The data obtained agree well with the quantum transitions of an isolated neodymium ion and a neodymium ion in glass [6, 7]. The wider absorption and reflection bands (see Figs. 4 and 5) of the ions is due to the fact that the bonding of the electrons with the nucleus in atoms is weakened in the glass phase, and the energy of visible light is sufficient for electrons to make a transition from the 4*f* into the 5*d* shell.

Ob"edinenie Gzhel' JSC conducted experimental-production tests for porcelain containing neodymium oxide. The color quality of the articles obtained was good.

In summary, the following conclusions can be drawn from the results of theoretical and experimental investigations:

with respect to the coloring power POW_F neodymium oxide is a weak pigment, which makes it possible to impart to white porcelain a soft light-blue and rose tone depending on the light source;

the optimal content of neodymium oxide in porcelain is 5 – 7%, which is sufficient for perceiving color duality — dichroism of porcelain;

porcelain containing neodymium oxide possesses a rose tone over the entire surface area of the article, and the color is independent of the firing conditions.

These properties of neodymium oxide make it a valuable pigment, despite its relatively high cost, in the production of household and art porcelain.

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